

SATURATED HYDROCARBON POLYMERIC BINDER FOR
ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAIN

PERIOD COVERED: January 1, 1968
March 31, 1968

This work was performed for the Jet Propulsion Laboratory,
California Institute of Technology, as sponsored by the
National Aeronautics and Space Administration under Contract
NAS 7-100

Report Edited By: James E. Potts

Contributors:

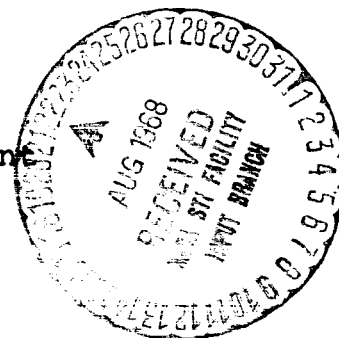
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Publication Date: April 20, 1968

Jet Propulsion Laboratory Contract No. 951210

Technically Managed By: H. E. Marsh, Jr. - JPL

UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS
Polymer Research and Development
Bound Brook, New Jersey



N 68-31729

(ACCESSION NUMBER)	(THRU)	(CODE)	(CATEGORY)
28	1	27	
(PAGES)			
28-96133			
(NASA CR OR TMX OR AD NUMBER)			

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TECHNICAL CONTENT STATEMENT

This report contains information prepared by Union Carbide Corporation, Chemicals and Plastics Operations Division, under J.P.L. subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology or the National Aeronautics and Space Administration.

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I. OBJECTIVE

Union Carbide Corporation, Chemicals and Plastics Operations Division, has agreed to assist the Jet Propulsion Laboratory, California Institute of Technology, on a level of effort basis, in the development of a new or improved polymeric binder for advanced solid propellant and hybrid propellant grains. The general objectives are described in Quarterly Report No. 1.

II. ABSTRACT

The continuous stirred autoclave reactor system has been modified by the addition of automated pressure controls. The reactor itself has been replaced by another unit with a higher pressure rating. The new system can operate effectively at 35,000 psi.

A melt process employing no solvent and using potassium hydroxide dispersed at 300°C in the polymer melt has been found to give rapid and quantitative elimination of HBr from ethylene/neohexene telomers with a minimum of rearrangement to vinylidene type C=C. Processes using solvents were either not as fast, gave a large amount of rearranged product or both.

A new series of telomers has been prepared, this group having ethylene and propylene as comonomers and having BrCCl₃, α-bromo isobutyric acid and its t-butyl ester as the telogens. A combination of low viscosity and very low penetration temperature make these telomers very attractive as solid propellant binder precursors.

III. SCOPE OF PROJECT

The scope of this work has been enlarged to include an examination of other copolymers of ethylene which offer the promise of a saturated hydrocarbon binder with greatly improved low temperature and viscosity properties.

IV. INTRODUCTION

In our last Quarterly Report we discussed the startup of operations in the continuous stirred autoclave reactor. Reaction conditions and product goals established during the exploratory phase of our effort were used as points of reference for ethylene/neohexene telomers synthesis in the continuous reactor. Effective control of telomer molecular weight was attained by suitable choice of reactor residence times and telogen concentration. Uniform products of high functionality were obtained from these runs.

We also reported the further improvement of the dehydrobromination/ozonolysis route for efficient conversion of Br to COOH endgroups in the telomers of ethylene/neohexene.

In this report we will present a detailed description of our continuous telomerization unit. We will also report a solvent free method for efficiently dehydrobrominating the terminal bromide in ethylene/neohexene telomers. This bulk polymer melt operation avoids the possibility of re-esterifying terminal COOH groups upon workup, and is also more practical on a larger scale than the previously used methods.

Exploratory batch telomerizations of ethylene with propylene in our small reactor have given telomer samples having very promising low temperature properties. In this report we will give the results of these telomerizations and will also describe the preparation of larger quantities of these new telomers in the continuous reactor.

V. TECHNICAL DISCUSSION

A. Modification of The Continuous Stirred-Autoclave Reactor

In section C of the technical discussion of our last Quarterly Report we described the use of a continuous stirred autoclave reactor for the preparation of ethylene neohexene copolymers by telomerization. The reactor itself was of 1.5 liter capacity and could operate at pressures up to 20,000 psi. We used this reactor to prepare telomers at rates between 30 and 150 grams per hour, depending upon the conditions employed. Control of the pressure was obtained by manual adjustment of a throttle valve which controlled rate of removal of product from the reactor.

We have recently replaced the original 20,000 psi reactor with another similar reactor rated at 40,000 psi, and have added automatic pressure control features which permit a more uniform operation.

Figure 1 shows a schematic drawing of the modified continuous reactor unit. The legend on the following page identifies the numbered components.

Essentially, the same procedure is followed with the new system as was used in our previous unit. The only differences are the automatic control of pressure and the higher pressure limit. The upper pressure limit is set by the pneumatic pressure transmitter (8 in Figure 1) which has a maximum pressure rating of 35,000 psi.

We will be conducting most of our telomerizations near this upper limit in order to maximize the rate of propagation. This will improve the productivity, and will allow a higher concentration of telogen to be used.

In subsequent discussion, our original system with the 20,000 psi rated reactor will be designated "Unit I" and the present system with an upper limit of 35,000 psi will be called "Unit II".

LEGEND FOR FIGURE 1.

1. Ethylene cylinder with regulator for maintaining constant feed pressure.
 2. Mixed feed cylinder with eductor tube.
 3. Scales, capacity 90 Kg. \pm 10 gms.
 4. Refrigerated bath, to -35°C .
 5. Pneumatic feed flow control via regulated rheostat for DC motor giving variable pump rpm.
 6. Triplex pumps, 60 mpsi max., 7/16" dia., pistons x 5/8" stroke.
 7. Emergency vent valve.
 8. Pneumatic pressure transmitter, to 35 mpsi.
 9. Pressure controller for emergency vent.
 10. Magnedrive autoclave, 1.5 liter capacity, 316 s.s. lined, 40 mpsi max., at 350°C , 3 each 6-bladed turbines equally spaced on agitator shaft, jacketed for heating by circulating heat transfer fluid.
 11. Air driven motor, up to 200 rpm.
 12. Pressure controller for motor valve 14.
 13. Temperature recorder, $0-500^{\circ}\text{C}$, IC TC, circular chart.
 14. Motor valve, to 50 mpsi at 100°F .
 15. Diverter valve*.
 - 16 and 17. Product receivers, stainless steel, 6 gal., capacity, to 300 psi.
 18. Diverter valve*, for vent gas.
- Not shown: Heat transfer system, 22.5 KW electrical heat for 25 gal. heat transfer medium (htm). Temperature controller-recorder for heat transfer system.

* Diverter valves operated by electrical switch in control room.

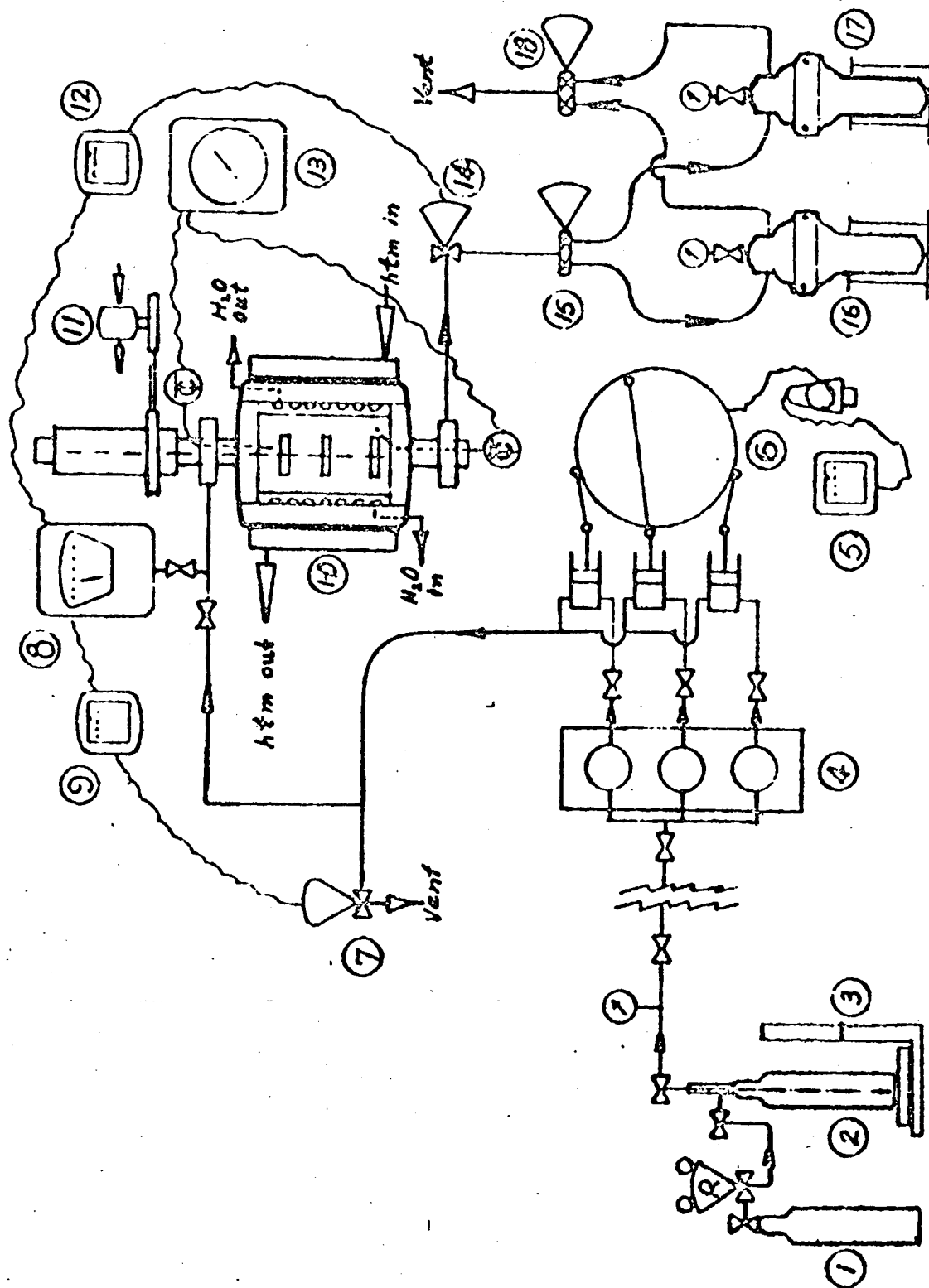


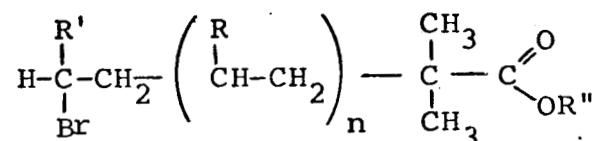
FIGURE 1. CONTINUOUS STIRRED AUTOCLAVE REACTOR, UNIT II

B. Ethylene/Neohexene Telomer Reaction

Studies: Dehydrobromination

During the past quarter we have continued our study of the conversion of telomer halogen functionality to COOH functionality. A major part of this study deals with the telomer dehydrobromination reaction itself.

All of the following results were obtained for ethylene/neohexene telomers where the telogens used were α -bromoisobutyric acid (CTAC) and its *t*-butyl ester (CTAD). The structure of these telomers is given by the formula below:



where R is H or *t*-butyl

R' is predominantly *t*-butyl

R'' is H, *t*-butyl, or methyl

Our previously reported procedure consisted of refluxing the telomer in a concentrated solution of KOH in *n*-butanol (100 g. per 500 ml. of solvent). The butanol was then removed by steam distillation and the product recovered by acidification with acetic acid and extraction into hexane or heptane, followed by evaporation to give the dehydrobrominated copolymer. This procedure satisfactorily eliminated all of the terminal halogen and gave a product with terminal double bonds. The terminal ester groups from the telogen or initiator were also saponified and converted to COOH.

This procedure, however, had a few drawbacks:

- 1) An inert atmosphere was necessary to avoid dark colored products, presumably arising from butanol oxidation.
- 2) Removal of all traces of butanol solvent was required prior to acidification and workup. This was to avoid re-esterification of the terminal COOH groups introduced by the telogen or initiator.
- 3) Small amounts of vinylidene type double bonds resulted from the dehydrobromination.

Since problems 1) and 2) resulted directly from the butanol used as the solvent and problem 3) might have been indirectly related to the solvent used, we conducted a series of experiments in which no butanol was used in most of the trials. The conditions used are summarized below:

- a) Base used: potassium acetate
Solvent used: molten potassium acetate
Temperature: 300°C

In this procedure the telomer is added to a flask containing molten potassium acetate at 300°C. For 3 g. of telomer, 50 g. of KOAc was used. The resulting solution was stirred under an inert atmosphere for 10 minutes and then allowed to cool. The solid reaction mixture was then taken up in water, made acidic with acetic acid and the telomer recovered by extraction with heptane.

- b) Base used: potassium hydroxide
Solvent used: n-butanol
Temperature: 117°C, reflux

This is the old procedure, previously discussed, with steam distillation used to completely remove the butanol upon workup.

- c) Base used: sodium hydroxide
 Solvent used: none
 Temperature: 250°C

In this procedure the telomer is heated to between 150 and 200°C under a stream of nitrogen, and an aqueous solution of a 2 to 3-fold amount (based upon total Br⁻ and -COOR equivalents in the telomer sample) of sodium hydroxide is added dropwise with stirring. After the addition is complete and all water has been driven off, the temperature is raised to 250°C and kept there for 10 min. Workup as in (a).

- d) Base used: potassium hydroxide
 Solvent used: none
 Temperature: 300°C

The same sequence of operations as in (c).

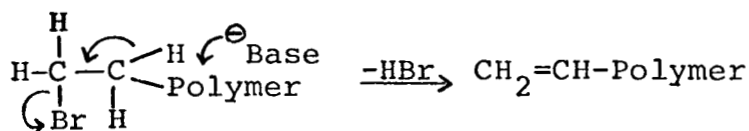
- e) Base used: potassium t-butoxide
 Solvent used: toluene
 Temperature: 110°C, reflux

In this procedure the telomer is refluxed for 65 hrs. under an inert atmosphere in a toluene solution containing a 2-fold amount (based upon total equivalents Br[⊖] and -COOH present in the telomer) of potassium t-butoxide, and the resulting aqueous suspension of the copolymer is acidified with acetic acid and the product is recovered by heptane extraction.

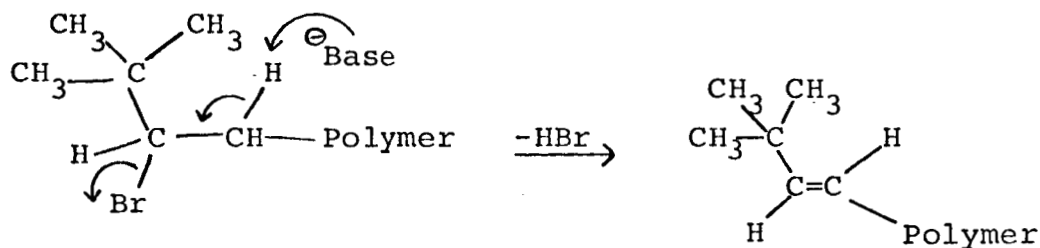
The products were recovered from all of these procedures in essentially quantitative yield as slightly cloudy light amber oils, giving a negative Beilstein test. Double bond formation was shown by the appearance of olefinic proton signals in the NMR Spectra as well as the characteristic hydrogen-carbon bond deformation bands in the fingerprint region of the infrared spectra. Strong absorption near 970 cm⁻¹ showed the presence of CH=CH (trans), and a much weaker absorption near 890 cm⁻¹ showed the presence of >C=CH_2 (vinylidene). The latter absorption was much more apparent in the spectra of products prepared with method "a" or "b".

Considering only the yield (nearly quantitative) and the residual halogen content (negative Beilstein test) of the final product, all four procedures gave equivalent results. However, the distribution of double bond types produced was different in each of the procedures evaluated. We observed an interesting correlation between the type of C=C functionality introduced and the polarity of the reaction medium. Table I shows the results we obtained when the products from the various dehydrobromination procedures were analyzed for double bond content by infrared spectroscopy.*

The vinyl content in all the examples shown can only arise from the loss of HBr by β -elimination from an ethylene end residue:

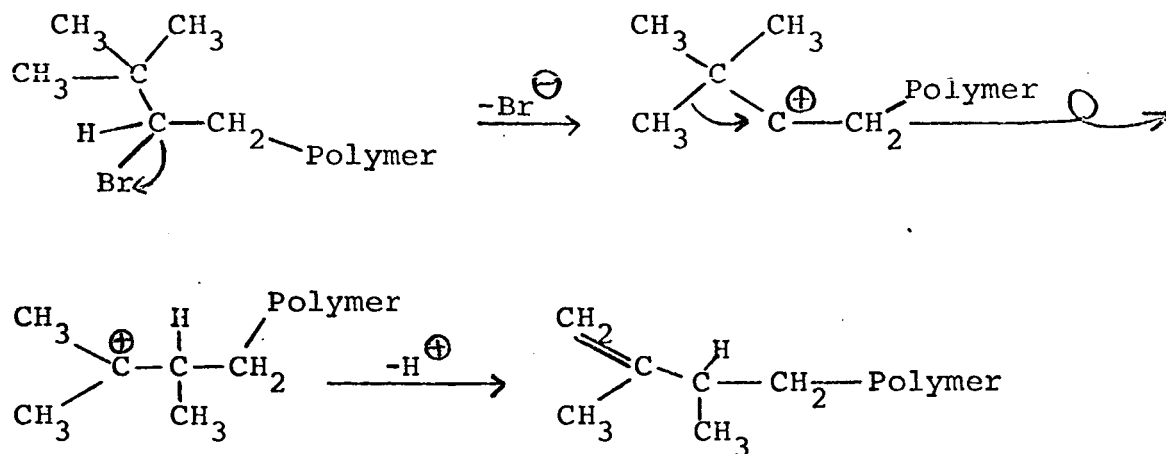


whereas, the vinylidene and the trans-internal double bonds can only arise from elimination of HBr from a neohexene residue. The trans-internal result from the β -elimination reaction which we have discussed in previous reports:



* See the Appendix for the method which was used in this analysis.

The vinylidene double bonds probably result from a unimolecular dissociation, followed by a carbonium ion rearrangement:



The carbonium ion formation is favored in highly polar reaction media which can support charge separation. Once formed, the neopentyl carbonium ion undergoes a facile 1, 2 methyl migration leading to the more stable tertiary carbonium ion, which in turn loses a proton to give the vinylidene functional group.

Our experiments are in accord with this generalization in that the greatest amount of vinylidene is formed in the highly polar molten potassium acetate medium of method "a". In methods "c", "d", and "e" the reaction media are non-polar and much less vinylidene is formed. Method "b" is intermediate in this respect.

Since vinylidene endgroups lead to methyl ketone functional groups upon ozonolysis, a subsequent oxidation step (using, for example, sodium hypobromite) is required following procedures "a" and "b" to obtain the highest possible COOH functionality. Because of this we favor the latter two methods. Method "d" is especially attractive, since no solvent is required, and since a complete reaction is obtained in very short reaction times.

TABLE I

Telomer Sample	Dehydrobromination Procedure Used	Percent of Total Double Bonds			Trans/Vinylidene
		Vinyl	Vinylidene	Trans-internal	
25-EMS-88	a) Molten KOAc	3	28	69	2.5
25-EMS-22	b) KOH/Butanol	4	23	73	3.2
25-EMS-40	c) NaOH/250°C No Solvent	4	13	83	6.4
8725-35-1	d) KOH/300°C No Solvent	0	11	89	8.1
25-EMS-88	e) K ^t BuO/Toluene	10	1	89	89

C. Ethylene/Propylene Telomers as
Saturated Amorphous Binder Precursors

1) Preparation

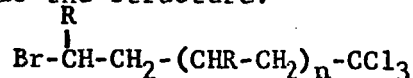
Previous to the last quarter, the scope of our program was restricted to the synthesis and evaluation of copolymers of ethylene with neohexene as saturated hydrocarbon binder precursors. An olefinic comonomer is necessary to prevent crystallization of the ethylene units in the polymer backbone, which leads to solid waxes, useless as propellant binders. Neohexene was the most attractive choice of the possible α -olefin comonomers because it contains no allylic hydrogen atoms. Other α -olefins, such as propylene or butene-1 were not seriously considered at the beginning of this program.

At that point we depended upon recombination of growing polymer radicals with initiator radicals (present in much higher than normal "catalytic" amounts) to provide functional groups upon the chain ends. The deleterious effect of chain transfer to comonomer upon the functionality of the product was to be avoided if at all possible.

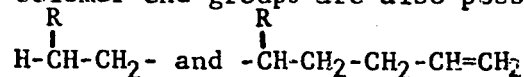
More recently however, we have been using extremely reactive chain transfer agents (telogens) to place the functional groups upon the chain ends. These telogens have an active halogen atom which is much more readily abstracted than an allylic hydrogen atom. In this environment, productive chain transfer, i.e., chain transfer leading to usable functional groups, may be expected to compete with chain transfer to monomer to such an extent that a product of useful functionality can be obtained.

To test out this hypothesis we tried a few small batch telomerizations of ethylene with propylene in which bromo-trichloromethane was used as the telogen.*

-
- * When BrCCl_3 is the telogen, the growing polymer radical abstracts a bromine to give a bromide terminated chain and a trichloromethyl radical which can initiate another polymer chain. The telomer which results has the structure:



To the extent that chain transfer to propylene can also occur, the following telomer end groups are also possible:



The first of these is of no value as a functional group, however the vinyl end group is a potential precursor to a COOH group.

Telomerization runs 24-EMS-134 and 136 were made using ethylene/propylene comonomers with BrCCl_3 telogen and dimethyl α, α' -azobisisobutyrate (DMAB) as initiator. The production and analytical data are summarized in Tables II and III. Functionality was determined from the halogen analyses and the molecular weight.

Our choice of telogen concentration was too high in these initial runs and telomers of very low molecular weight resulted. The total halogen functionalities were high however, 2.31 and 1.84 groups per molecule, and the penetration temperatures were far lower than any previously encountered in this program, -100 and -95°C .

These results encouraged us to try a series of continuous telomerizations at lower effective concentration of telogen. We also substituted the more useful telogen α -bromoisobutyric acid or its *t*-butyl ester in place of the Br-CCl_3 . The production and analytical data are given in Tables IV and V.

The first three runs, 25-EMS-103, 104 and 105, were made in the Unit I reactor using α -bromoisobutyric acid telogen. These runs were made at 20,000 psi pressure, the upper limit of this reactor. Holdup time was varied by using different feed rates at the same pressure. In these runs we found that slightly higher production rates are obtained at the expense of lower overall conversion if high feed rates are used. This is illustrated by run 25-EMS-103 in which a production rate of 201 grams of telomer per hour was obtained at 2.26% conversion of monomers. At this rate, over 3 kilos of telomer can be produced in a single run of three 8 hr. shifts (allowing ample time for start-up and shut-down operations).

The next two runs, 25-EMS-106 and 27-EMS-19, were also made in the Unit I reactor at 20,000 psi, but using the *t*-butyl ester telogen. The conditions used were very similar to those chosen for run #25-EMS-104, and the productivity obtained was nearly identical. In this respect the two telogens are interchangeable. The α -bromo ester telogen is less active as a chain transfer agent, however, and as a result the products from run 25-EMS-106 and 27-EMS-19 have higher molecular weights than 25-EMS-104, even though the molar ratio of telogen to monomers was the same, .0015.

TABLE IIETHYLENE/PROPYLENE TELOMERS

Batch Run #	24-EMS-134	24-EMS-136
<u>Initial Charge</u>		
BrCCl ₃ , gms.	2.72	3.42
Solvent, gms.	11.4	14.0
AlBN, gms.	0.1	0.13
Ethylene, gms.	330	384
Propylene, gms.	420	528
<u>Fed During Reaction</u>		
BrCCl ₃ , gms.	41.1	30.8
Solvent, gms.	172.2	129.5
AlBN, gms.	1.91	1.14
<u>Reaction Conditions</u>		
Temp., °C	90	90
Pressure, mpsi		
Initial	4.20	10.40
Maximum	9.25	15.00
Time, hrs.	4.25	6.42
<u>Productivity</u>		
Yield, gms.	35	49
Conversion, %	4.85	5.48
Rate, %/M.	1.14	.85

TABLE IIIETHYLENE/PROPYLENE TELOMERS

Run #	24-EMS-134	24-EMS-136
<u>Physical Properties</u>		
Brookfield Viscosity, cps	-	163
Specific Viscosity, 80°C	.009	.011
Vitrification Temperature	below-80°C	below-80°C
Penetration Temperature	-100°C	-95°C
<u>Analytical Data</u>		
Molecular Weight*	343	421
Bromine, Wt. %†	27.07	17.94
Chlorine, Wt. %†	35.76	22.58
<u>Functionality</u>		
Bromine (Br)	1.16	0.95
Chlorine (CCl ₃)	1.15	0.89

* By vapor phase osmometry in benzene.

† By Paar bomb combustion followed by potentiometric titration with silver nitrate.

TABLE IV

ETHYLENE/PROPYLENE TELOMERS

Continuous Run # Continuous Unit #	25-EMS-	103 I	104 I	105 I	106 I	27-EMS-19(d) I	34 II
<u>Charge, Wt. % on Total</u>							
Benzene		10.53			→ 11.49	→	10.89
Ethylene		47.87			→ 44.83	→	46.29
Propylene		40.80			→ 42.56(c)	42.56(d)	40.84
Telogen		.66(d)			→ .96(b)	→	1.82
DMAB		.14			→ .15	→	.14
Mole Ratio, Telogen/Monomers		.0015			→	→	.0031
Vapor Pressure of Feed, 25°C, psi		480	540	575	540	510	540
Wt. Feed Used, gms.		5345	5502	2185	7056	6539	7080
<u>Reaction Conditions</u>							
Temp., °C		123	110	100	110	110	105-107
Pressure, mpsi		20					→ 35
Nominal Holdup Time, min.		5.1	13.2	29.4	13.9	15.9	18.8
Avg. Feed Rate, gms/m		12,070	3377	1689	3377	3269	3078
<u>Productivity</u>							
Yield, gms.		107	136	73	175	172	281
Conversion, %		2.26	2.79	2.63	2.80	2.97	4.56
Rate, g/m		201	97.1	41.8	93.1	86.0	122

(a) α-bromoisobutyric acid

(b) t-butyl -bromoisobutyrate

(c) Propylene used contained ~25% impurities, mostly propane.

(d) Repeat of 106. Pure propylene used.

TABLE V

ETHYLENE/PROPYLENE TELOMERS

Continuous Run #	25-EMS-	103	104	105	106	27-EMS-19	34
<u>Physical Properties</u>							
Brookfield Viscosity, cps		2805	2912	3156	6830	5620	5000
Specific Viscosity, 80°C		-	-	-	-	.031	.033
Penetration Temperature, °C		-74	-69	-73	-66	-	-
<u>Analytical Data</u>							
Molecular Weight		744(a)	775(a)	684(a)	1189(b)	1190(b)	1074(b)
Bromine, Wt. %		7.50	6.53	7.73	3.84	3.96	5.49
Neutralization Equiv.		1137	1156	960	-	-	-
<u>Functionality</u>							
Bromine (Br)		.70	.63	.66	.57	.59	.74
Carboxyl (COOH)		.65	.67	.71	-	-	-

(a) By V.P.O. in THF

(b) By V.P.O. in Benzene

The last ethylene/propylene telomerization run, 27-EMS-34, was made in the recently set up Unit II reactor, operating at 35,000 psi. A lower molar ratio of telogen to monomers was used in this run to compensate for the higher propagation rate at the higher pressure so as to obtain the same target molecular weight, near 1000 g/mole. The higher pressure also had a beneficial effect upon the productivity. 4.56% conversion was obtained at a rate of 122 g. telomer per hour, the highest of the whole series.

2) Physical Properties

The telomers produced with α -bromoisobutyric acid telogen were amber colored, pourable oils (the color is a peculiarity of this particular telogen, and may be due to HBr loss from the telogen itself - addition of a trace of alkali causes the color to disappear). When the *t*-butyl ester of α -bromoisobutyric acid was used instead the telomers obtained had a light straw color.

Two important conclusions can be drawn from the physical property data given in Table V:

- a) The Brookfield viscosity of the carboxyl terminated ethylene/propylene telomers is significantly lower than that of other saturated carboxyl terminated binders at comparable molecular weights.
- b) The very low penetration temperatures suggest that cured binders prepared from ethylene/propylene carboxyl terminated liquids will have excellent low temperature properties.

Figure 2 shows the room temperature Brookfield viscosities of saturated carboxyl terminated liquid binders plotted as a function of their molecular weights (a log-log plot was used for convenience and to more nearly linearize the data). The data for carboxyl terminated ethylene/neohexene telomers is that which we reported in our previous Quarterly Report for telomers prepared in the Unit I continuous stirred autoclave reactor at 20,000 psi using α -bromoisobutyric acid telogen (CTAC).

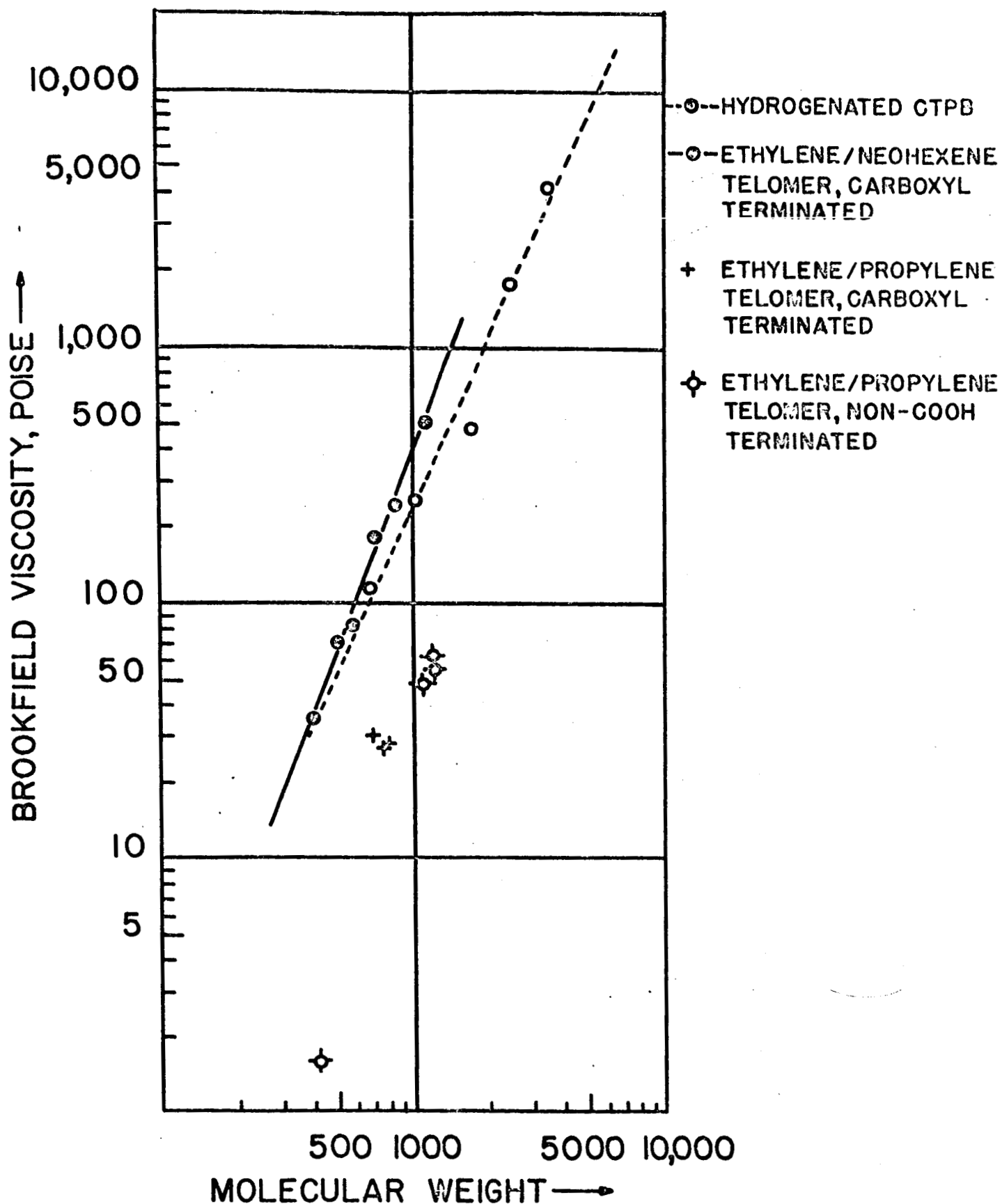


FIGURE 2. BROOKFIELD VISCOSITY—MOLECULAR WEIGHT RELATIONSHIPS

The data for hydrogenated carboxyl terminated polybutadiene was taken from Figure 1, page 22, of the final report (February 1966) by D. E. Johnson and A. J. DeMilo on contract AF04(611)-10386 for the Air Force Rocket Propulsion Laboratory at Edwards, Calif. These saturated binders contained ethyl branches resulting from the 1, 2-vinyl content (around 30% of the total unsaturation) of the original polybutadiene.

The data for ethylene/propylene telomers is taken from Tables III and V of the present report. Three of the samples have COOH endgroups and may be compared with the other carboxyl terminated saturated binders.

The lower viscosity of the ethylene/propylene telomers is probably due to the decreased bulk of the methyl branches in the new telomers as compared with the ethyl branches in hydrogenated carboxyl terminated polybutadienes, or the *t*-butyl branches in ethylene/neohexene copolymers. This lower viscosity should facilitate propellant formulation and casting of grains at lower temperatures than are conventionally required.

Figure 3 shows the results obtained when the penetration temperatures of the ethylene/propylene telomers were plotted as a function of the reciprocal of the molecular weight. A reasonably good linear fit was obtained, which when extrapolated to $1/\bar{M}_n=0$, gave a penetration temperature near -50°C at infinite molecular weight. At $\bar{M}_n=1000$, T_p is -67°C .

3) Functionality

The high functionalities which were achieved in the low molecular weight telomers of BrCCl_3 (see Table III) have not yet been obtained in the higher molecular weight telomers of α -bromoisobutyric acid or its *t*-butyl ester (see Table V). The lower telogen concentration employed in the more recent runs was selected in order to attain a higher molecular weight. Under these conditions, chain transfer to propylene becomes more probable as the telogen concentration is reduced.

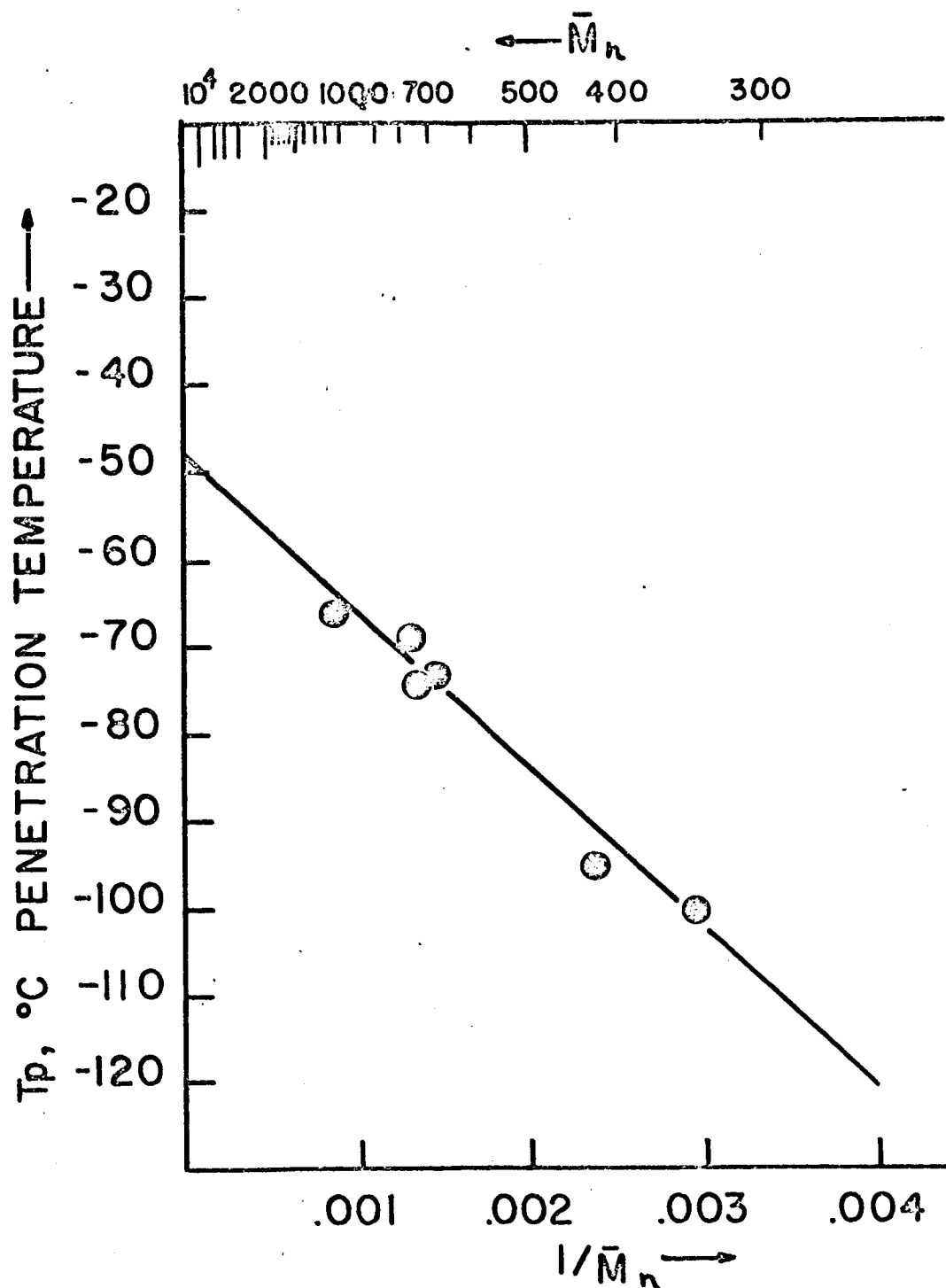


FIGURE 3. MOLECULAR WEIGHT DEPENDENCE OF THE PENETRATION TEMPERATURE OF ETHYLENE/PROPYLENE TELOMERS

An exception to this trend is found in run 27-EMS-34. This is the first continuous run in the Unit II reactor. *t*-Butyl α -bromoisobutyrate was used as the telogen and the reactor internal pressure was 35,000 psi. The telomer produced in this run had the highest functionality in the whole series of continuous runs: 0.74 bromine per molecule.

This higher functionality may be directly attributed to the higher reactor pressure. This leads to a higher propagation rate and thus requires that the telogen to monomer molar ratio be increased from .0015 to .0031 in order to control the molecular weight. At this higher telogen concentration, relatively less chain transfer to propylene monomer could occur, hence the higher functionality.

Telomerization at very high reactor pressures is undoubtedly the best means available to us to obtain higher functionality and productivity in the preparation of ethylene/propylene copolymers.

4) Chemical Modification - Br to COOH

Since the new ethylene/propylene telomers have only recently been prepared and characterized, chemical modification studies directed toward conversion of the bromine functionality into carboxyl functionality are just beginning. However, some experiments have been completed which point out the greater reactivity toward displacement reactions of the terminal bromide in the ethylene/propylene telomers.

Dehydrobromination of telomer samples 25-EMS-103, 104 and 105 using NaOH in the polymer melt at 250°C led to products containing no bromine (negative Beilstein test) after short reaction periods (15 min.). However, judging from the infrared spectra of the products, less than the theoretical double bond content was produced.

Ozonolysis of the dehydrobrominated telomers in acetic acid/carbon tetrachloride solution at 0°C, followed by oxidative workup using peracetic/performic acid mixtures gave products containing no residual unsaturation and having enhanced COOH contents.

To illustrate these findings with a specific example, telomer sample 25-EMS-104 originally had 0.63 Br per molecule and .67 COOH per molecule. Oxygen analysis indicates 0.83 O₂ per molecule, the difference being the ester groups derived from the initiator. The total functionality is thus 1.46. After dehydrobromination, ozonolysis, and oxidation a product was obtained having a molecular weight of 740 and a neutralization equivalent of 588 and hence containing 1.26 COOH per molecule. This represents a net gain of .43 COOH group per molecule, about 2/3 the expected amount.

The infrared spectrum of the product exhibited both carboxylic acid and ester carbonyl bands. However, after saponification, no significant increase in COOH content was observed as determined by titration. This suggests that the ester groups seen in the infrared spectrum were acetate or formate groups derived from terminal hydroxyl groups. These, in turn, were most probably the result of a direct displacement of bromide by hydroxyl during the dehydrobromination step. This reaction was not significant in the dehydrobromination of ethylene/neohexene telomers due to the highly hindered nature of the secondary neopentyl bromide end groups.

When molten potassium acetate was used, both as the solvent and the base, for the dehydrobromination reaction (method a in part B of this report) more evidence was provided which pointed out the greater reactivity of the terminal halogen toward displacement. Strong acetate absorptions and weak c=c absorptions were present in the infrared spectrum of the (Beilstein negative) product resulting from molten potassium acetate treatment of 25-EMS-104. These show that nucleophilic displacement of bromide can readily occur in this system.

We have planned for the coming quarter, several experiments on the ethylene/propylene telomers which failed when they were applied to ethylene/neohexene telomers due to the very hindered nature of the terminal halogen:

- 1) $\ominus \text{SCH}_2\text{COOR}$ displacement of $\text{Br} \ominus$
- 2) $\text{S} \ominus$ coupling, displacing 2 $\text{Br} \ominus$
- 3) $\text{CN} \ominus$ displacement of $\text{Br} \ominus$, followed by hydrolysis to COOH.

The greater reactivity of the halogen end groups in the new telomers may make the above reactions useful for changing $\text{Br} \ominus$ to COOH in the ethylene/propylene telomers.

VI. PLANS FOR FUTURE WORK

In the quarter to come we plan to carry out additional telomerizations of ethylene with propylene at the highest pressure attainable in the present equipment so as to obtain higher functionality products. Meanwhile, laboratory work on the displacement of the terminal bromide functionality using very good nucleophiles such as mercaptides (e.g. $K^+ \ominus S-CH_2COOCH_3$) will be carried out on the available ethylene/propylene telomers.

Concurrent with this we plan to try several procedures designed to enrich the functionality of carboxyl terminated prepolymers already on hand. Counter current solvent extraction methods will be evaluated, and if successful, will be used to prepare difunctional binders from lower functionality ethylene/propylene copolymers for curing studies.

VII. NEW TECHNOLOGY

A. Penetration Temperature Method

In our Quarterly Report #7 we reported a new method for measurement of the glass transition temperature of liquid binders. This method was dependent upon the fact that a weighted penetrometer needle will not penetrate a binder in the hard glassy state below its glass transition temperature, but will after the binder has been warmed above T_g . This new measure of T_g has been designated " T_p " for penetration temperature.

Figure 4 shows the essential working components of the apparatus which we use for measuring T_p . The key element is the penetrometer needle, A. We used a penetrometer needle of the type specified by A.S.T.M. method D-5, weight 2.5 grams. The needle is attached to a freely moving vertical shaft, B, of a rack and pinion type precision penetrometer conforming to A.S.T.M. method D-5. The shaft has a weight of 47 1/2 grams. Weights, C, of 50, 100 or 150 grams may be loaded on the top of the shaft C. For our purposes 150 grams worked well. A fixed collar on shaft B bears upon an arm connected to a freely moving vertical rack, D, which engages pinion, E, which drives a pointer, F, providing visual read-out of the position of needle A. Scale divisions correspond to 1/10 mm. movement of A, therefore estimates of position can readily be made to the nearest 1/50 mm.

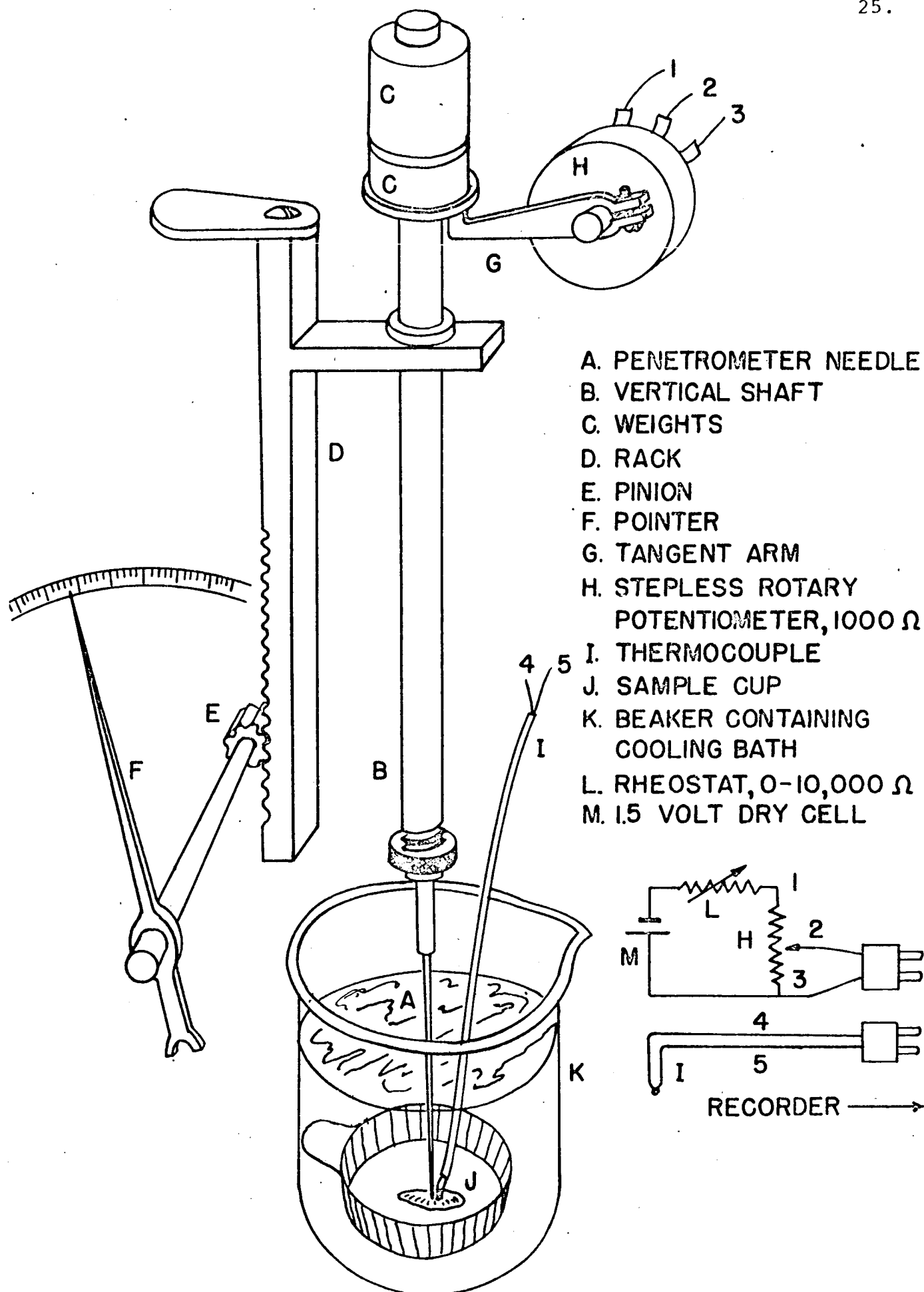


FIGURE 4. PENETRATION TEMPERATURE APPARATUS

To provide for greater ease in determining the penetration temperature we have added a tangent arm, G, which contacts the lower side of the flange supporting weights C. This tangent arm drives the shaft of a 1000 Ω one turn stepless potentiometer which, in conjunction with rheostat L, serves as a voltage divider for a 1.5 volt dry cell. The rheostat is adjusted so as to give an output voltage between 2 and 6 millivolts over the normal range of needle movement corresponding to about 5 mm. This voltage is connected to one of the 6 channels of a Leeds & Northrop Speedomax recorder giving a 10 inch strip chart record of 0 to 8 millivolts. This system gives a nearly linear readout of the penetrometer needle position.

We simultaneously record the output of an iron-constantan thermocouple which is immersed in the methanol cooling bath, K, in contact with the pre-chilled binder sample in an aluminum foil sample cup, J.

Below T_p , needle A rests on the top of the sample and a straight line is recorded on one channel of the recorder corresponding to this position. Another channel is meanwhile recording the rising sample temperature. When T_p is reached, the needle suddenly begins to penetrate the sample. This is recorded as an abrupt end point on the strip chart and may be compared with the corresponding temperature later on. When the needle reaches the bottom of the sample and strikes the cup J, another straight line is produced. Figure 5 shows a typical result for an ethylene propylene telomer.

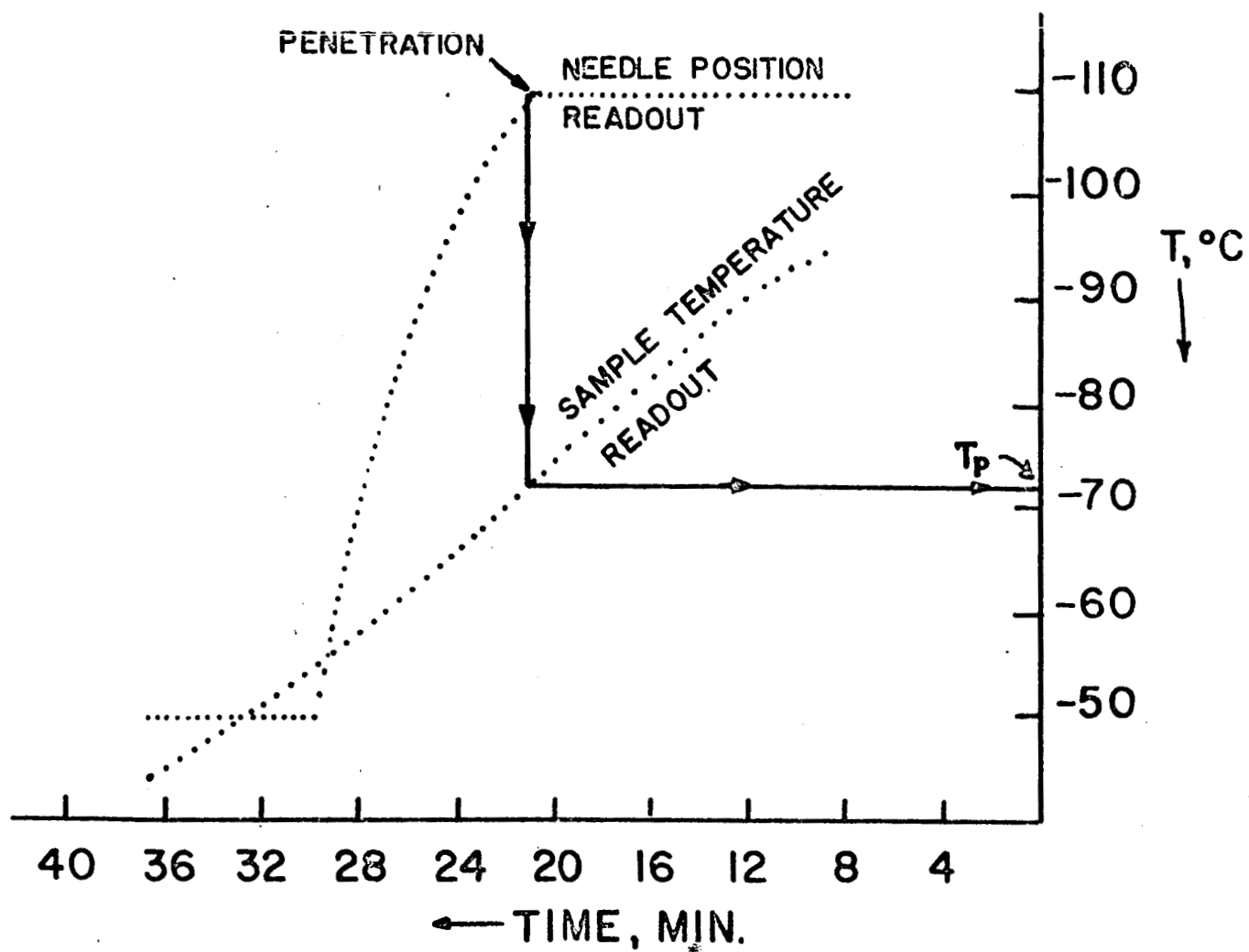


FIGURE 5. RECORDER OUTPUT FOR T_p DETERMINATION

VIII APPENDIX

Infrared Analysis for Double Bonds

Our method for determining the type of unsaturation present is based upon the C-H out of plane wagging vibrations in the infrared spectrum in the vicinity of 900 cm^{-1} . Anderson and Seyfried (Anal. Chem., 20, 998) give a table summarizing the absorption coefficients for various functional groups, including several types of double bonds. The pertinent values are summarized below:

Functional Group	Structure	Absorption @ Maximum μ cm^{-1}		Absorption Coefficient
Vinyl	$-\text{CH}=\text{CH}_2$	10.98	909	50.3
Vinylidene	$>\text{C}=\text{CH}_2$	11.24	889	43.1
Trans-internal	$\text{H} > \text{C}=\text{C} < \text{H}$	10.36	965	35.6

From the infrared absorption at the peak maximum, and the absorption coefficients given above, the weight fraction (W.F.) of a given functional group can be calculated from:

$$\text{W.F.} = A / (10 \times b \times c \times p \times K)$$

where A = absorption at peak maximum

b = cell thickness in mm

c = volume fraction of sample (1 for neat samples)

p = density of sample

K = absorption coefficient from table above.

However, the cell thickness is difficult to determine accurately in the demountable gasket-spaced-cells which we have found to be most useful for liquid polymers, and the density of a given sample is seldom known with enough accuracy. Accordingly, for the present work, we have only determined the relative values of the weight fractions of the different double bond types in a given sample as measured from a single scan of a nominally 1 mil (.0254 mm.) thick preparation of the neat liquid polymer. Each relative value is proportional to the ratio A/K for the functional group in question, since in a single scan, b, c, and p remain constant. Therefore, if

$$R_1 = A_{\text{vinyl}}/50.3$$

$$R_2 = A_{\text{vinylidene}}/43.1$$

$$R_3 = A_{\text{trans}}/35.6$$

$$R_T = R_1 + R_2 + R_3$$

Then the percent of total double bonds which are vinyl is $100R_1/R_T$, the percent vinylidene is $100R_2/R_T$ and the percent trans-internal is $100R_3/R_T$.